

(63) **PATENT ABSTRACTS OF JAPAN**

(11)Publication number : 11-264037

(43)Date of publication of application : 28.09.1999

(51)Int.Cl. C22C 9/00
 B21B 3/00
 C22F 1/08
 H01B 1/02
 H05K 1/09
 // C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00
 C22F 1/00

(21)Application number : 10-088223

(71)Applicant : NIPPON MINING & METALS CO
LTD

(22)Date of filing : 18.03.1998

(72)Inventor : MAKI TETSUO

(54) COPPER ALLOY FOIL

(57)Abstract:

PROBLEM TO BE SOLVED: To provide Cu-Fe-P series copper alloy foil having sufficient strength and electrical conductivity and moreover excellent in productivity.

SOLUTION: This foil is the one having a compsn. contg., by weight, 0.05 to 3.5% Fe and 0.01 to 0.4% P, furthermore contg., at need, one or two kinds of 0.05 to 5% Zn and 0.05 to 3% Sn, moreover contg., at need, one or more kinds among Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B by 0.01 to 2% in total, and the balance Cu, in which the dimensions of inclusions are regulated to $\leq 10 \mu\text{m}$, and also, the number of the inclusions with 5 to $10 \mu\text{m}$ dimensions is regulated to < 50 pieces/mm² in the cross-section parallel to rolling. It is suitable as a copper alloy foil material high in reliability in use for printed circuit boards and in a semiconductor packaging field such as IC tape carriers.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

(19)日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11)特許出願公開番号

特開平11-264037

(43)公開日 平成11年(1999) 9月28日

(51)Int.Cl. ⁶	識別記号	F I	
C 2 2 C	9/00	C 2 2 C	9/00
B 2 1 B	3/00	B 2 1 B	3/00 L
C 2 2 F	1/08	C 2 2 F	1/08 B
H 0 1 B	1/02	H 0 1 B	1/02 A
H 0 5 K	1/09	H 0 5 K	1/09 A
審査請求 未請求 請求項の数 5 F D (全 5 頁) 最終頁に続く			

(21)出願番号 特願平10-88223

(22)出願日 平成10年(1998) 3月18日

(71)出願人 397027134

日鉱金属株式会社

東京都港区虎ノ門二丁目10番1号

(72)発明者 牧 哲生

神奈川県高座郡寒川町倉見三番地日鉱金属

株式会社倉見工場内

(74)代理人 弁理士 倉内 基弘 (外1名)

(54)【発明の名称】 銅合金箔

(57)【要約】

【課題】 十分な強度および電気伝導度を有し、さらには生産性にも優れたCu-Fe-P系銅合金箔を提供すること。

【解決手段】 Feを0.05~3.5%およびPを0.01~0.4%含有し、必要に応じて0.05~5%のZnおよび0.05~3%のSnのうち1種または2種を含有し、さらに必要に応じてMg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InおよびBのうち1種以上を総量で0.01~2%含有し、残部がCuからなり、介在物の大きさが10μm以下であり、かつ5~10μmの大きさの介在物個数が圧延平行断面で50個/mm²未満であることを特徴とする。プリント配線基板用およびICテープキャリア等半導体実装分野の用途において信頼性の高い銅合金箔材料として好適である。

【特許請求の範囲】

【請求項1】 重量割合で、0.05～3.5%のFeおよび0.01～0.4%のPを含有し、残部がCuおよびその不可避的不純物からなり、そして介在物の大きさが10μm以下であり、かつ5～10μmの大きさの介在物個数が圧延平行断面で50個/mm²未満であることを特徴とする銅合金箔。

【請求項2】 重量割合で、0.05～3.5%のFeおよび0.01～0.4%のPを含有し、さらに0.05～5%のZnおよび0.05～3%のSnのうち1種または2種を含有し、残部がCuおよびその不可避的不純物からなり、そして介在物の大きさが10μm以下であり、かつ5～10μmの大きさの介在物個数が圧延平行断面で50個/mm²未満であることを特徴とする銅合金箔。

【請求項3】 重量割合で、0.05～3.5%のFeおよび0.01～0.4%のPを含有し、さらにMg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InおよびBのうち1種以上を総量で0.01～2%含有し、残部がCuおよびその不可避的不純物からなり、そして介在物の大きさが10μm以下であり、かつ5～10μmの大きさの介在物個数が圧延平行断面で50個/mm²未満であることを特徴とする銅合金箔。

【請求項4】 重量割合で、0.05～3.5%のFeおよび0.01～0.4%のPを含有し、さらに0.05～5%のZnおよび0.05～3%のSnのうち1種または2種を含有するとともに、さらにまたMg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InおよびBのうち1種以上を総量で0.01～2%含有し、残部がCuおよびその不可避的不純物からなり、そして介在物の大きさが10μm以下であり、かつ5～10μmの大きさの介在物個数が圧延平行断面で50個/mm²未満であることを特徴とする銅合金箔。

【請求項5】 鋳塊に所定の圧延と熱処理を施して得た中間素材に対し、材料温度が300～700℃の温度で1～10時間の時効処理を行った後、最終の圧延で0.1mm以下の厚さに仕上げたことを特徴とする、請求項1～4のいずれかに記載した銅合金箔。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】 本発明は、フレキシブルプリント配線基板用およびICテープキャリア等半導体実装の用途に好適な、強度および電気伝導性に優れた銅合金箔に関するものであり、特に介在物の大きさおよび介在物の個数を規制したCu-Fe-P系銅合金箔に関する。

【0002】

【従来の技術】 有機物を基材としたプリント配線基板は、ガラスエポキシ、紙フェノール基板を構成材料とする硬質銅張積層板（リジット）と、ポリイミド、ポリエ

ステル基板を構成材料とする可撓性銅張積層基板（フレキシブル）とに大別され、プリント配線基板の導電材としては主として銅箔が使用されている。銅箔はその製造方法の違いにより電解銅箔と圧延銅箔に分類される。上記プリント配線基板のうち、プリント配線板のより高密度回路化による多層板化および高可撓性が要求されるフレキシブルプリント回路基板は、樹脂基板に銅箔をラミネートし、接着剤あるいは加熱加圧により一体化して形成される。使用される銅箔としては、タフピッチ銅または無酸素銅の圧延銅箔が多く用いられており、近年では、高密度実装の有効な手段として、ビルドアップ基板と呼ばれる多層配線基板が多く用いられている。

【0003】 さらに、プリント配線基板の一部はテープキャリア、TAB（テープ・オートメーテッド・ボンディング）リードとして、半導体チップの実装に使用されている。半導体チップの実装の分野においては、近年、その実装密度の向上のためBGA（ボール・グリッド・アレイ）化、CSP（チップ・サイズ・パッケージ）化が進められている。これにより、面積当たりの端子数は増加するが、同時に端子は狭ピッチとなるため、実装する基板にも高密度の配線基板が必要となる。高密度化実現のための有効な手段として、半導体実装分野においても多層基板が用いられている。

【0004】 一方、製造工程においては、箔の厚さが薄くなると、歩留よく圧延することが困難となってくる。特に、介在物等の内部欠陥は、圧延時に破断を生じまたピンホールを生じる原因となるため、生産性を低下させ、ひいては製造コストの増大を招く。従って、素材には介在物の少ないことが望まれる。近年、電子機器銅合金のような高い強度と導電性を要求される用途には、析出型銅合金が使われるケースが多い。Cu-Fe-P系銅合金は、高強度と高導電率とを併せ持つ代表的な析出型銅合金であり、電子機器用材料として実用化されている。この合金においては、時効析出過程において銅マトリックス中に微細なFeあるいはFe-P系化合物が析出することにより強度と導電率が上昇する。

【0005】

【発明が解決しようとする課題】 前述のプリント基板は、（1）組み立て時に曲げた状態で固定されて使用されるもの、（2）駆動系統（例えばプリンターのヘッド部分、ハードディスク内の駆動用回路基板等）に使用され、1万回～100万回以上の屈曲が繰り返されるもの、等に用いられる。近年の電子機器の小型化と高密度化に伴い、プリント基板自体も小型化が要求され、純銅箔では強度が不足するため、部品の加工および組み立て時に切断あるいは変形といった問題が生じる。また純銅は耐熱性が著しく低いため、銅箔を樹脂基板にラミネートする際の加熱によって変形、断線という問題が発生し、信頼性が低下するという欠点があった。

【0006】 半導体チップの実装の分野においては、搭

載されるチップの回路ルールの微細化が進展しており、「0.1~0.2μmルール」が開発されている。0.1~0.2μmルールの場合、チップ裏面につける金あるいはアルミバンプのピッチは40μm程度になり、40μmピッチのバンプを接合するには、基板の配線ピッチを15μm以下にする必要がある。配線のピッチを15μm以下にするためには、基板に使用される銅箔の板厚を14μm以下にする必要がある。これは、銅箔の板厚をピッチ以下にしないと、エッチング、組み立て加工ができないためである。しかし、従来の圧延銅箔では、板厚が14μm以下になると強度の不足からIRB（インナーリード・ボンディング）時に切断あるいは変形といった問題が生じる。従って上記要請に対処しうる十分な強度とさらに十分な電気伝導性を持った材料が求められている。

【0007】上記要求に対し、ある種の添加元素を加えた銅合金を用いることは有効な手段の一つではあるが、銅合金を用いるということだけでは必ずしも十分な強度は得られず、加えて元素の添加により基板の他の必要特性である電気伝導度の低下といった問題が生じる。また、前述したCu-Fe-P系合金においては、銅マトリックス中に微細なFeあるいはFe-P系析出粒子が生じることにより、強度と導電率が上昇するが、反面強度の向上に寄与しない粗大な晶出物あるいは析出物が残存し易く、また添加元素の活性が高いために、酸化物、硫化物、珪化物等が発生し易いため、マトリックス中にこれらの比較的大きな粒子が分散した組織となり易いという結果を生むことになっている。Cu-Fe-P系合金を銅合金箔材料として実用化するに当たって、これらの粗大な粒子が残存すると、圧延時に破断、ピンホール

【0008】

【課題を解決するための手段】そこで、本発明者らは、金属箔として適する銅合金箔の研究を重ねたところ、Cu-Fe-P系合金の成分調整を行った上で、必要に応じて、Znおよび/またはSn、さらにはMg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、Inおよび/またはBを含有させると共に、製造条件を制御・選定してマトリックス中の析出物、晶出物、酸化物、硫化物、珪化物等の介在物の分布の制御を行うことにより、合金箔として好適な素材を提供できることを見出した。本発明は、上記知見を基にして完成されたものであり、銅合金においてFeを0.05~3.5重量%（以下百分率は特記しない限り重量%を意味する）およびPを0.01~0.4%含有し、必要に応じて0.05~5%のZnおよび0.05~3%のSnのうち1種または

2種を含有し、さらに必要に応じてMg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InおよびBのうち1種以上を総量で0.01~2%含有し、残部がCuおよびその不可避的不純物からなり、介在物の大きさが10μm以下であり、かつ圧延平行断面で5~10μmの大きさの介在物個数が50個/mm²未満であることを特徴とする、プリント配線基板用やICテープキャリア用の箔として十分な強度と電気伝導性を兼備せしめ、さらには生産性も良好な銅合金箔に関する。

10 【0009】本発明において、用語「介在物」とは、铸造時の凝固過程以降、すなわち凝固後の冷却過程、熱間圧延後の冷却過程および時効焼鈍時に固相のマトリックス中に析出反応で生じる析出物、铸造時の凝固過程の偏析により生じ一般に粗大である晶出物、並びに溶解時の溶湯内での反応により生じる不純物である酸化物および硫化物など、本合金の顕微鏡観察によりマトリックス中に観察される粒子を包括するものとして使用する。「介在物の大きさ」は、介在物を顕微鏡観察下でその介在物を含む最小円の直径をいう。「介在物の個数」とは、材料の圧延平行断面を顕微鏡観察により、多数箇所において実際に数えた単位平方mm当たりの介在物個数である。

【0010】

【発明の実施の形態】次に本発明において銅合金の成分組成を前記の如くに限定した理由をその作用とともに説明する。

【0011】(Fe) Feは、単独であるいはPと金属間化合物を形成して、合金の強度、耐熱性を向上させる作用があるが、その含有量が0.05%未満であると所望の高強度が得られない。一方、3.5%を超える割合でFeを含有させると、加工性が低下するとともに導電性が著しく低下し、さらには粗大なFe粒子が母相中に残留する。この結果、圧延時の破断、ピンホール発生等により生産性の低下を招くことになる。こうした理由で、Feの含有量を0.05%以上3.5%以下と定めた。

【0012】(P) Pは、Feと金属間化合物を形成して、導電性を下げずに強度を向上させるが、0.01%未満ではその効果がなく、他方0.4%を超えると加工性が著しく低下するとともに導電率が著しく低下することから、P含有量は0.01%以上0.4%以下と定めた。

【0013】(Zn) Znは、溶解铸造時の脱酸剤として作用するとともに、半田接合部の耐熱性を改善する効果があるが、その含有量が0.05%未満ではその効果が顕著でなく、一方Znの含有量が5%を超えると、導電率の低下が著しくなることから、Zn含有量は0.05%以上5%以下と定めた。

【0014】(Sn) Snには、合金の強度を確保する作用があるが、その含有量が0.05%未満では強度の

向上が十分でなく、一方Sn含有量が3%を超えると導電率の低下が著しくなるとともに、合金の熱間加工性を低下させることから、Sn含有量は0.05%以上3%以下と定めた。

【0015】(Mg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InまたはB) Mg、Co、Pb、Zr、Cr、Mn、Al、Ni、Si、InまたはBには、いずれも等しく上記銅合金の強度を改善する作用があるので必要により1種または2種以上の添加がなされる。しかし、その含有量が総量で0.01%未満であると強度改善の効果は得られず、一方総含有量が2%を超えると導電性が著しく低下することから、これらの含有量を総量で0.01%以上2%以下と定めた。

【0016】(介在物) この合金系ではマトリックス中に介在物の粒子が存在することがある。この合金に必要な強度を得るための介在物は小さいが、0.5μmを超える粗大な介在物は強度に寄与しないばかりか、特に粗大なものは圧延工程において破断やピンホールの原因となり、生産性を著しく低下させる。このような不具合を起こさないためには、この粗大な介在物の大きさの上限を10μmとし、圧延平行断面における5~10μmの大きさの介在物個数を50個/mm²未満とすればよい。

【0017】次に、この合金を得るための製造工程について説明する。所望の強度および電気伝導性を得るためには、素材の調質状態は時効処理状態である必要がある。この時効処理は、強度、電気伝導性を向上させるために必要であるが、時効処理温度は300~700℃にする必要がある。300℃未満では時効処理に時間がかかり、経済的でなく、他方700℃を超えるとFeが固溶してしまい、時効による強度および電気伝導性の向上が生じないためである。また、次に冷間圧延により所望の板厚に仕上げるわけであるが、冷間圧延後の箔の厚さは、100μm(0.1mm)以下とすることが望まし*

*く、通常の使用形態を想定した圧延銅合金箔の好ましい厚さは、例えば0.035mm、0.07mm、0.018mmまたは0.010mmである。

【0018】

【実施例】以下、実施例および比較例により本発明をさらに詳しく説明する。

(実施例及び比較例) 高周波溶解炉にて表1に示す各種成分組成の銅合金を溶製し、厚さ20mmのインゴットに鑄造した。次に、このインゴットを800~950℃温度で厚さ8mmまで熱間圧延を行い、表面のスケール除去のため面削を施した後、冷間圧延により厚さ2mmの板とした。その後、350~900℃の温度で1時間の焼鈍を行った後、0.5mmまで冷間圧延した。そしてさらに、400~600℃の温度で5時間の時効を行った後、冷間圧延で厚さ0.018mmの箔とした。

【0019】このようにして得られた各合金箔につき諸特性の評価を行った。なお表中には従来合金としてタフピッチ銅を併記した。「強度」については引張試験機において引張強さを測定した。「電気伝導性」は導電率(%IACS)によって示した。「耐熱性」の評価は種々の温度で30分間加熱し、引張強さが加熱前の強度と十分軟化した時の強度の間になる温度を軟化温度として求めた。介在物個数は、材料の圧延平行断面を顕微鏡で観察し、多数箇所において実際に数えた単位平方mm当たりの大きさ5~10μmの介在物個数である。また、厚さ0.018mm、幅450mm、長さ5000mの箔を作製し、生産性の評価も行った。「生産性」は圧延工程中の破断発生状況および製品段階でのピンホールの発生状況で評価した。「破断」については、破断が発生しなかった場合を○、破断した場合を×とした。

「ピンホール」については1000mm当たりの直径0.5mm以上のピンホールの発生個数を計測した。

【0020】

【表1】

表1 本発明合金および比較例

		成 分 (重量%)					引 張 強 さ N/mm ²	導電 率 % IACS	軟化 温度 ℃	介在物 数 個/mm ²	破断 の有無	ピンホール 発生個数 個/1000m
		Fe	P	Zn	Sn	副 成 分						
本 発 明 合 金	1	0.5	0.03	—	—	—	540	75	400	0	○	1
	2	2.16	0.02	0.11	—	—	535	83	450	19	○	3
	3	0.93	0.04	—	0.7	—	590	58	460	11	○	3
	4	1.7	0.04	0.2	1.1	—	620	51	420	4	○	1
	5	2.29	0.03	2.15	0.14	0.06 Mg	580	55	430	21	○	6
	6	1.68	0.04	—	—	0.08 B	580	68	430	6	○	2
	7	1.68	0.04	2.48	—	0.23 Co	590	55	400	9	○	4
	8	2.13	0.03	0.42	—	0.06 Zr	610	61	520	11	○	2
比 較 合 金	1	4.26	0.05	—	—	0.06 Mg	640	35	500	73	×	19
	2	0.05	0.05	0.82	3.56	—	610	16	440	14	○	5
	3	2.08	—	—	—	0.26 Zr	470	55	420	51	×	15
	4	3.54	0.41	—	0.31	0.05 Al	610	21	410	98	×	27
従来材		タフピッチ銅					380	97	140	—	○	2

【0021】表1からわかるように、本発明合金箔は優れた強度、導電率および耐熱性を有している。介在物個数が少ないため、ピンホールの発生個数は少なく、最大で6個である。一方、比較合金の No. 1は、本発明合金に対し、Feが高いために導電率が劣る。比較合金 No. 2はSnが高いため導電率が劣る。比較合金 No. 3はPを含有していないために強度が劣る。比較合金 No. 4は、Fe、Pとも高いために導電率が劣る。また比較例 No. 1、3、4は、介在物個数が多いために製造工程中*30

*で破断が発生し、ピンホールの個数が増加した例である。

【0022】

【発明の効果】以上説明したように、本発明によれば、優れた強度と電気伝導性および耐熱性をも有し、さらには生産性にも優れた銅合金箔が得られ、本合金箔は、プリント配線基板用およびICテープキャリア等半導体実装分野の用途において信頼性の高い銅合金箔材料として好適である。

フロントページの続き

(51) Int. Cl.⁶

// C 22 F 1/00

識別記号

6 0 2
6 0 3
6 2 2
6 6 1
6 8 5
6 8 6
6 9 1
6 9 4

F I

C 22 F 1/00

6 0 2
6 0 3
6 2 2
6 6 1 A
6 8 5 Z
6 8 6 A
6 9 1 B
6 9 1 C
6 9 4 A

(19) JAPANESE PATENT OFFICE (JP)

(12) Official Gazette for Laid-Open Patent Applications (A)

(11) Japanese Laid-Open Patent Application (Kokai) No. 11[1999]-264,037

(43) Laying-Open Date: 28 September 1999

(51) Int.Cl. ⁶	Ident. Symbols	FI	
C22C 9/00		C22C 9/00	
B21B 3/00		B21B 3/00	L
C22F 1/08		C22F 1/08	B
H01B 1/02		H01B 1/02	A
H05K 1/09		H05K 1/09	A

Request for Examination: Not yet requested

Number of Claims: 5 FD (Total of 5 pages)

Continued on last page

(21) Application No.: 10[1998]-88,223

(22) Application Date: 18 March 1998

(71) Applicant: 397027134
Nikko Metals Company, Ltd.
10-1 Totanomom 2-chome, Minato-ku, Tokyo-to

(72) Inventor: Tetsuo Maki
c/o Kurami Plant
Nikko Metals Company, Ltd.
3 Kurami, Samukawa-achi, Koza-gun, Kanagawa-ken

(74) Agent: Motohiro Kurauchi, Patent Attorney (And 1 Other)

(54) [Title of the Invention] A Copper Alloy Foil

(57) [Abstract]

[Problem] To provide a Cu-Fe-P copper alloy foil which has sufficient strength and electrical conductivity and which is also of superior productivity.

[Means of solution] It is characterized in that it contains 0.05 to 3.5% Fe and 0.01 to 0.4% P, and, as required, that it contains one or two of 0.05 to 5% Zn and 0.05 to 3% Sn, and, further, as required, in that it contains a total amount of 0.01 to 2% of one or more of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B, in that the remainder is Cu, in that the size of inclusions is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/mm² in a rolled parallel cross section. It is suitable as a copper alloy foil material of high reliability for printed circuit boards and for uses in the field of semiconductor mounting such as IC tape carriers.

[Claims]

[Claim 1] A copper alloy foil characterized in that it contains, in terms of weight ratios, 0.05 to 3.5% Fe and 0.01 to 0.4% P, in that the remainder is comprised of Cu and unavoidable impurities thereof, in that the size of inclusions is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/mm² in a rolled parallel cross section.

[Claim 2] A copper alloy foil characterized in that it contains, in terms of weight ratios, 0.05 to 3.5% Fe and 0.01 to 0.4% P, further, in that it contains either one or both 0.05 to 5% Zn and 0.05 to 3% Sn, in that the remainder is comprised of Cu and unavoidable impurities thereof, in that the size of inclusions is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/mm² in a rolled parallel cross section.

[Claim 3] A copper alloy foil characterized in that it contains, in terms of weight ratios, 0.05 to 3.5% Fe and 0.01 to 0.4% P, further, in that it contains a total amount of 0.01 to 2% of one or more of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B, in that the remainder is comprised of Cu and unavoidable impurities thereof, in that the size of inclusions is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/mm² in a rolled parallel cross section.

[Claim 4] A copper alloy foil characterized in that it contains, in terms of weight ratios, 0.05 to 3.5% Fe and 0.01 to 0.4% P, further, in that it contains either one or both 0.05 to 5% Zn and 0.05 to 3% Sn, in that it contains a total amount of 0.01 to 2% of one or more of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and

B, in that the remainder is comprised of Cu and unavoidable impurities thereof, in that the size of inclusions is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/ mm^2 in a rolled parallel cross section.

[Claim 5] A copper alloy foil as described in any one of claims 1 to 4, further characterized in that the intermediate material obtained by performing specified rolling and heat treatments on ingots is subjected to aging treatment for 1 to 10 hours at a material temperature of 300 to 700°C and in that it is finished to a thickness of less than 0.1 mm in the final rolling.

[Detailed Description of the Invention]

[0001]

[Technological field of the invention] This invention relates to a copper alloy foil that is suited for use in flexible printed circuit boards and semiconductor mountings such as IC tape carriers and that has superior strength and electrical conductivity. In particular, it relates to Cu-Fe-P copper alloy foil in which the size of inclusions and the number of inclusions are controlled.

[0002]

[Prior art] Printed circuit boards in which organic substances are the substrates are generally divided into hard copper stretched laminated board (rigid) in which glass epoxy and paper phenol substrates are used as the structural materials and flexible copper stretched laminated board (flexible) in which polyimide and polyester substrates are used as the structural materials. Copper foil is used primarily as the conductive material in printed circuit boards.

Copper foil is classified as electrolytic copper foil and rolled copper foil depending on the method of its manufacture. Of the aforementioned printed circuit boards, flexible circuit boards, which are required to have multiple-layer boards because their circuits are of higher density than those of rigid printed circuit boards and must have high flexibility, are formed by laminating copper foil on a resin substrate and by making a single structure by means of an adhesive agent or by heating under increased pressure. Rolled copper foil of tough pitch copper or oxygen-free copper is frequently used as the copper foil. In recent years, multiple-layer wiring boards called "buildup" substrates are frequently used as effective means of high density mounting.

[0003] Some printed wiring boards are used in the mounting of semiconductor chips as tape carrier and TAB (tape automated bonding) leads. In the field of mounting of semiconductor chips, there have in recent years been advances in BGA (ball grid arrays) and CSP (chip size packages) for the purpose of increasing mounting density. By this means, the number of terminals relative to area is increased. However, at the same time, the terminals are of narrow pitch, for which reason high density wiring substrates are also necessary in substrates that are mounted. Multiple-layer substrates are used in the field of semiconductor mounting as an effective means for producing higher density.

[0004] On the other hand, rolling with good yields is difficult in the manufacturing process when the thickness of the foil is very thin. In particular, internal defects such as inclusions are the cause of occurrence of fractures during rolling or of the occurrence of pinholes, for which reason, productivity is

decreased, and, in turn, manufacturing cost is increased. Consequently, it is desirable for there to be few inclusions in the materials. In recent years, there are many cases in which precipitated copper alloy is used for applications in which high strength and conductivity are required as in alloys for electronic devices. Cu-Fe-P copper alloys are representative precipitated copper alloys which have both high strength and high conductivity and have been put into practical use as materials for electronic devices. In this alloy, strength and conductivity are increased by the fact that fine Fe or Fe-P compounds are precipitated in the copper matrix in the aging precipitation process.

[0005]

[Problems the invention is intended to solve] The printed circuit boards described above are used in (1) cases in which they are fixed and used in a bent state during assembly and (2) cases in which they are used in drive systems (for example, head components of printers, circuit boards for drives inside hard disks, etc.) and in which bending is repeated from 10,000 to over 1 million times. As electronic devices have become smaller and of high density in recent years, there has also been a demand to make the printed board itself smaller. Because pure copper foil is of insufficient strength, the problems have arisen of breaking or deformation during processing and assembly of components. Further, because pure copper is of markedly low heat resistance, the problems have arisen of deformation and disconnection due to heating at the time of laminating the copper foil on the resin substrate and there has been the drawback that reliability is decreased.

[0006] In the field of mounting of semiconductor chips, there have been advances in producing the circuit rule of the chip that is mounted on a finer scale and "0.1 to 0.2 μm rules" are being developed. In the case of 0.1 to 0.2 μm rule, the gold or aluminum "bump" pitch on the back face of the chip is on the order of 40 μm . In order to connect a bump of 40 μm pitch, it is necessary for the wiring pitch of the substrate to be made to less than 14 μm . The reason for this that etching, assembly and processing cannot be performed when the plate thickness of the copper foil is not made less than 14 μm . However, when the plate thickness of conventional rolled copper foil is less than 14 μm , its strength is not sufficient, for which reason the problems arise of breakage or deformation during IRB (inner reed bonding). Consequently, there is a demand for a material having sufficient strength and also sufficient electrical conductivity to meet the aforementioned demands.

[0007] The use of a copper alloy to which various elements have been added is an effective means for meeting the aforementioned demands. However, the problems arise that sufficient strength cannot necessarily be obtained solely by using copper alloy and there is a decrease in electrical conductivity, which is another required characteristic of substrates, due to the addition of elements. In the Cu-Fe-P alloys described above, strength and conductivity are increased as a result of the fact that fine Fe or Fe-P particles are produced in the copper matrix. However, on the other hand, coarse crystallized material or precipitated material that does not contribute to an improvement in strength tends to remain and the activity of the added elements is increased, for

which reason there is the result that a texture is readily formed in which these comparatively large particles are dispersed in the matrix. When these large, coarse particles remain they are the cause of the occurrence of breakage and pinholes in putting Cu-Fe-P alloys to practical use as copper alloy foil materials. For this reason, productivity is decreased, and, in turn, manufacturing costs are increased. This invention was developed for the purpose of solving the problems described above and has the objective of providing Cu-Fe-P copper alloy foil that has sufficient strength and electrical conductivity and that is of superior productivity.

[0008]

[Means for solving the problems] Accordingly, when the inventors conducted repeated research on copper alloy foil suited as metal foil, they discovered that a suitable material could be provided as an alloy foil, in performing adjustment of the components of Cu-Fe-P alloys, as required, by having them contain Zn and/or Sn, and, further, Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and/or B and by controlling and selecting manufacturing conditions to control the distribution of inclusions such as precipitated material, crystallized material, oxides, sulfides and silicides in the matrix. This invention was perfected on the basis of the aforementioned information and relates to copper alloy foil which is endowed with both sufficient strength and electrical conductivity for use as foil for printed circuit boards and for IC tape carriers and that is also of excellent productivity, which is characterized in that the alloy foil contains 0.05 to 3.5 weight % Fe (percentage hereafter signifying weight % unless otherwise

specified) and 0.01 to 0.4% P, and either one or both of 0.05 to 5% Zn and 0.05 to 3% Sn as well as further, as required, that it contain a total amount of 0.01 to 2% of one or more of Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In and B, in that the remainder is comprised of Cu and unavoidable impurities, in that the size of the impurities is less than 10 μm and in that the number of inclusions of a size of 5 to 10 μm is less than 50/ mm^2 in a rolled parallel cross section.

[0009] In this invention, the term "inclusion" is used as a comprehensive term for particles that can be observed in the matrix by microscopic observation of this alloy, such as precipitated material that is produced in precipitation reactions in the solid-phase matrix in processes subsequent to solidification at the time of casting, i.e., the cooling process after solidification, the cooling process after hot rolling and during aging and annealing, crystallized material that is produced by segregation in the solidification process at the time of casting and that is generally coarse, and oxides and sulfides which are impurities that are produced by reactions in baths during melting. The expression "size of inclusion" refers to the diameter of the smallest circle that circumscribes an inclusion when the inclusion is observed under the microscope. The expression "number of inclusions" is the number of inclusions per mm^2 that is actually counted in a large number of sites by microscopic observation of a rolled average cross section of material.

[0010]

[Mode of execution of the invention] Next we shall explain the reason that the component composition of the copper alloy in this invention is limited as described above, as well as its action.

[0011] (Fe) Fe, by itself, or by forming an intermetallic compound with P, acts to increase the strength and heat resistance of the alloy. When its content is less than 0.05 %, the desired high strength cannot be obtained. On the other hand, when it contains Fe in a proportion exceeding 3.5%, processing capacity is decreased, conductivity is markedly decreased and coarse Fe particles remain in the matrix phase. As a result, productivity is decreased due to the occurrence of fracture and pinholes during rolling. For these reasons, the content of Fe is set from 0.05% to 3.5%.

[0012] (P) P forms an intermetallic compound with Fe and causes an increase in strength without lowering the conductivity. With less than 0.01%, this effect does not occur. On the other hand, when it exceeds 0.4%, processing capacity is markedly decreased and conductivity is also markedly decreased, for which reason the P content is set from 0.01% to 0.4%.

[0013] (Zn) Zn acts as a deoxidizing agent at the time of melting and casting and has the effect of improving the heat resistance of solder junctions. When its content is less than 0.05%, its effect is not marked. On the other hand, when the Zn content exceeds 5%, there is marked decrease in conductivity. For these reasons, the Zn content is set from 0.05% to 5%.

[0014] (Sn) Sn has the action of assuring the strength of the alloy. When its content is less than 0.05%, the increase in strength is not sufficient. On the

other hand, when the Sn content exceeds 3%, conductivity is markedly decreased and hot-processing capacity is decreased. For this reason, the Sn content is set from 0.05% to 3%.

[0015] (Mg, Co, Pb, Zr, Cr, Mn, Al, Ni, Si, In or B) all have the action of improving the strength of the aforementioned copper alloy. As required, one or two or more of these elements may be added. However, when the total content is less than 0.01%, the effect of improving the strength is not obtained. On the other hand, when the content exceeds 2%, there is a marked decrease in productivity. For this reason, the total content is set from 0.01% to 2%.

[0016] (Inclusions) Particles of inclusions are present in the matrix in this alloy system. These are small inclusions in the alloy for the purpose of obtaining the required strength. However, coarse inclusions exceeding $0.5\text{ }\mu\text{m}$ do not contribute to strength, and coarse inclusions in particular are the cause of fractures and pinholes in the rolling process, with productivity being markedly decreased. In order to eliminate this problem, the upper limit on the size of coarse inclusions should be set to $10\text{ }\mu\text{m}$ and the number of inclusions of a size of $5\text{ to }10\text{ }\mu\text{m}$ in rolled parallel cross sections should be less than $50/\text{mm}^2$.

[0017] Next, we will explain the manufacturing process for obtaining this alloy. It is necessary that the tempering of the material is an aging treatment for the purpose of obtaining the desired strength and electrical conductivity. This aging treatment is necessary for the purpose of increasing strength and electrical conductivity and it is necessary for the aging treatment temperature to be 300 to 700°C . When it is less than 300°C , the aging treatment takes time. This is not

economical. On the other hand, when it exceeds 700°C, the Fe goes into solid solution and an increase in strength and electrical conductivity do not occur as a result of aging. Next, finishing is performed to the desired board thickness by cold rolling. It is desirable that the thickness of the foil after cold rolling be less than 100 μm (0.1 mm). Desirable thicknesses for rolled copper alloy foil which is presumed to be in states of ordinary use are, for example, 0.035 mm, 0.07 mm, 0.018 mm or 0.010 mm.

[0018]

[Examples] We shall now describe this invention in further detail by means of examples and comparative examples.

(Examples and comparative examples) Copper alloys of the component compositions shown in Table 1 were melted in a high-frequency melting furnace and were cast into ingots of 20 mm in thickness. Next, these ingots were subjected to hot rolling to a thickness of 8 mm at a temperature of 800 to 950°C and surface "shaving" was performed for the purpose of removal of surface scale, after which a board was made of a thickness of 2 mm by cold rolling. Following that, annealing was performed for 1 hour at a temperature of 350 to 900°C, after which it was cold rolled to 0.5 mm. Further, aging was performed for 5 hours at a temperature of 400 to 600°C, after which it was made to foil of a thickness of 0.018 mm by cold rolling.

[0019] Evaluations were made of the properties of each of the alloy foils that were obtained in this way. The table also includes the findings for tough pitch copper as a conventional alloy. Tensile strength was determined as

"strength" with a tensile testing machine. "Electrical conductivity" was indicated by conductivity (% IACS). Evaluation of "heat resistance" was found by heating for 30 minutes at various temperatures and by taking the temperature at which tensile strength is intermediate between the strength before heating and the strength when it is sufficiently softened as the softening temperature. The number of inclusions was found by observing a rolled parallel cross section of the material under the microscope and is the number of inclusions of a size of 5 to 10 μm per mm^2 that is actually counted in a large number of sites. Foil of 0.018 mm in thickness, 450 mm of width and 5000 m in length and productivity was also evaluated. "Productivity" was evaluated by the state of occurrence of fractures in the rolling process and by the state of occurrence of pinholes in the product stage. When "fractures" did not occur, an evaluation of O was given and when fractures occurred an evaluation of X was given. "Pinholes" were evaluated by the number of occurrences of pinholes of greater than 0.5 mm in diameter per 1000 m.

[0020]

[Table 1]

Table 1. Alloys of This Invention and Comparative Examples

	Components (weight %)					Tensile strength N/mm ²	Conductivity % IACS	Softening temperature °C	Number of inclusions/m ²	Presence or absence of fracture	Number of occurrences of pinholes/1000 m
Alloys of this invention	Fe	P	Zn	Sn	Secondary component						
1	0.5	0.03	--	--	--	540	75	400	0	O	1
2	2.16	0.02	0.11	--	--	535	63	450	19	O	3
3	0.93	0.04	--	0.7	--	590	58	460	11	O	3
4	1.7	0.04	0.2	1.1	--	620	51	420	4	O	1
5	2.29	0.03	2.15	0.14	0.06 Mg	580	55	430	21	O	6
6	1.68	0.04	--	--	0.08 B	580	68	430	6	O	2
7	1.68	0.04	2.48	--	0.23 Co	590	55	400	9	O	4
8	2.13	0.03	0.42	--	0.06 Zr	610	61	520	11	O	2
Comparison alloys											
1	4.26	0.05	--	--	0.06 Mg	640	35	500	73	X	19
2	0.05	0.05	0.82	3.56	--	610	16	440	14	O	5
3	2.08	--	--	--	0.26 Zr	470	55	420	51	X	15
4	3.54	0.41	--	0.31	0.05 Al	610	21	410	98	X	27
Conventional material:	Tough pitch copper					380	97	140	--	O	2

[0021] As can be seen from Table 1, the alloy foils of this invention had superior strength, conductivity and heat resistance. Because the number of inclusions was small, the number of occurrences of pinholes was small, with a maximum of 6 being found. On the other hand, the conductivity of Comparison Alloy 1 was inferior to that the alloys of this invention because the Fe content was high. The conductivity of Comparison Alloy 2 was inferior because of the high Sn content. The strength of Comparison Alloy 3 was inferior because it did not contain P. The conductivity of Comparison Alloy 4 was inferior because of the

high Fe and P contents. Fractures occurred in Comparative Examples 1, 3 and 4 in the manufacturing process because there were large numbers of inclusions and there was an increase in the number of pinholes.

[0022]

[Effect of the invention] As described above, by means of this invention, copper alloy foil that has superior strength, electrical conductivity and heat resistance and that is also of superior productivity can be obtained. This alloy foil is ideal as a copper alloy foil material of high reliability for printed circuit boards and for uses in semiconductor mounting fields such as IC tape carriers.

[Continued from front page]

(51) Int.Cl. ⁶	Ident. Symbols	FI	
// C22F 1/00	602	C22F 1/00	602
	603		603
	622		622
	661		661A
	685		685Z
	686		686A
	691		691B
			691C
	694		694A